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Doklady Akademii Nauk SSSR, Vol LXXI, No 2, 1950.

INVESTIGATION OF ISOTOPIC EXCHANGE OF IODINE  
BETWEEN SODIUM IODIDE AND ETHYL IODIDE IN AN ALCOHOL SOLUTION

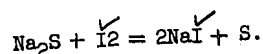
M. B. Neyman and R. V. Protsenko  
Presented by Acad N. N. Semenov  
16 Jan 1950

The method for concentrating radioactive isotopes suggested in 1934 by Szillard and Chalmers (1) in the case of concentrating  $I^{128}$  presupposes the absence of an exchange reaction between  $C_2H_5I$  and  $I^-$ . The question of the exchange between ethyl iodide and  $NaI$  in various solvents has been qualitatively studied by a number of researchers (2-5), who showed that the exchange proceeds slowly in alcohol solutions at low temperatures, and more rapidly at 100 degrees centigrade.

In 1942-43 two investigations (6, 7) were published in which the exchange between ethyl iodide and  $NaI$  in alcohol solutions was studied quantitatively. The 25-minute isotope of iodine  $I^{128}$  was used in these investigations, and for that reason the duration of the kinetic experiments was limited to several hours.

In this study, a mixture of long-lived radioactive isotopes of iodine was used, a fact which permitted more lengthy experiments to be conducted and also made it possible to expand the investigation into the field of low temperatures. The technique of the preparation and extraction of radioactive isotopes of iodine has been described in previous articles (8, 9) by Neyman and other collaborators.

Active sodium iodide was prepared according to the reaction:

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The liberated sulfur was filtered off, and the NaI containing inactive NaI was dissolved to form a 0.2 N solution in alcohol. Before initiating the kinetic experiment, this solution was mixed with an equal volume of a 0.2 N alcohol solution of ethyl iodide. The solutions were first heated or cooled to the temperature of the experiment.

Therefore, the experiment was conducted with solutions in which  $[NaI] = [C_2H_5I] = 0.1$  mol per liter. The small flasks containing the solutions were placed in a thermostat and the temperature was kept constant.

While the reaction was in progress, samples were taken and rapidly cooled, after which separation of the mixture was accomplished by shaking it up with benzene. Then, after separation of the water layer containing dissolved  $I^-$  ions, precipitation with  $AgNO_3$  was carried out. The ethyl iodide of the benzene layer was subjected to hydrolysis, after which the radiiodine was transferred into  $AgI$ . A Geiger-Mueller counter was used to investigate the  $AgI$  precipitate.

In all of the experiments, a part of the NaI to be mixed with ethyl iodide was precipitated with  $AgNO_3$ , and the active precipitate of  $AgI$  used as a control.

Results of the experiments performed in connection with this study at temperatures of 10, 20, 30, 40, and 80 degrees centigrade are given in the following table:

Kinetics of Exchange of Iodine between NaI and  $C_2H_5I$  at Different Temperatures ( $[NaI] = [C_2H_5I] = 0.1$  mol per liter)

Temp in °C	Temp in hr	Activity			Indicator	k.10 <sup>4</sup> liter mol/second
		$C_2H_5I$	NaI	$EtI$		
10	5	17	265	282	282	0.23
	10	19	244	263	270	
	15	20	227	247	249	
	20	21	201	222	231	
	24	21	201	222	231	
20	10	48	153	201	208	0.92
	17	59	120	179	180	
	24	53	87	140	136	
	24	53	87	140	136	
30	2	49	177	226	228	2.15
	4	54	163	217	219	
	6	64	149	213	213	
	8	69	139	208	209	
	10	71	133	204	206	
	16	50	60	110	112	
	20	49	55	104	104	
	24	46	48	94	97	
	24	46	48	94	97	
40	3	78	155	223	243	4.2
	5	75	123	198	200	
	10	71	81	152	148	
	12	65	68	133	142	
	12	65	68	133	142	
80	5 min.	50	138	188	180	153
	10 "	78	104	182	182	
	20 "	90	94	184	182	

If the reaction of isotopic exchange investigated in this instance is bimolecular, its rate constant can be expressed by the following formula:

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$$k = \frac{1}{(a+b)t} \ln \frac{1}{1-(1+\frac{b}{a})x/c} \quad (1)$$

In the present case, where  $a = [C_2H_5I] = b = [NaI] = 0.1$ , formula (1) is reduced to the form:

$$k = \frac{11.5}{t} \lg \frac{1}{1-2x/c} \quad (2)$$

where  $c$  is the total activity of the iodine (equal to the activity of the control) and  $x$  is the activity of the ethyl iodide.

Results of the experiments of this study are depicted on a graph the coordinates of which are  $\frac{1}{1-2x/c}$  and  $t$ .

As concerns the measurement of the magnitude  $x/c$  of isotopic exchange of  $C_2H_5I$  and  $NaI$  with time, the experimental points after being plotted lie on straight lines originating from the 0 point of the graph, which fact verifies the applicability of formula (2) to the reaction investigated. Values for the constants of the rate of isotopic exchange, derived from the slopes of the lines plotted are given in the last column of the above table.

To determine the energy of activation of the exchange reaction investigated here, the values for the constants were plotted in a graph with the coordinates  $\lg k$  and  $1,000/T$ . The points lie on a straight line along the slope of which may be found the value  $E = 19,000$  cal/mol. This quantity, within the limits of error for the experiments, corresponds with the values for energy of activation found in the works (6, 7).

If, based on the equation for the constant of the rate of the bimolecular reaction

$$k = P \frac{N_0}{1000} \sigma^2 \sqrt{\frac{8\pi RT M_1 M_2}{M_1 + M_2}} e^{-E/RT} \quad (3)$$

it is assumed that the value for the steric factor  $P = 0.1$ , and the values for  $k$  and  $E$  determined by Neyman and Protzenko are substituted, then a plausible value for the effective diameter  $\sigma \cong 3.10^{-8}$  cm is obtained.

[The graphs described above are available in the original document in CIA.]

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